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Determination of Total Sulfur in Gasoline by Gas Chromatography with a Flame Photometric Detector

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Total sulfur in gasoline is determined by gas chromatography with a flame photometric detector. The analysis time is less than 5 min with a detection limit of 0.002% S (by weight) and a precision of ±10% for duplicate results by the same operator. The main source of error is the imprecision of injection of very small sample volumes (0.1–0.4 μl). Gasoline samples with a sulfur concentration of up to 0.12% sulfur can be analyzed without dilution or sample preparation.

Analyses for sulfur in gasoline is a routine determination in refineries and petroleum oriented laboratories. The standard methods used for this analysis are American Society for Testing and Materials (ASTM) methods D1266 (Lamp Method) (*1*) and D-2622 (X-Ray Spectrographic Method) (*2*). The primary disadvantage of the Lamp Method is the time required for analysis; an analyst may be able to analyze, at most, 11 samples plus a blank in an 8-h period. Although the x-ray spectrographic method is fast, it also has the disadvantages of being expensive and of requiring a highly trained operator.

The specificity and sensitivity of the flame photometric detector (FPD) for sulfur compounds has been well documented (*3–5*). It therefore constitutes the basis for the method described below (Figure 1).

EXPERIMENTAL

Apparatus. A Perkin-Elmer Model 900 Gas Chromatograph (GC) was equipped with an FPD and control unit from Perkin-Elmer. In addition, a gas mixing device (Figure 2) made of glass with a volume of 60 ml was installed in the oven instead of a column. This gas mixing device is not commercially available and was fabricated from glassware on hand in the laboratory. Any gas mixing device that is close to the same volume (50–70 ml) should work as well. A Hamilton Co. No. 7001 syringe was used for sample injection. The data readout was via a Perkin-Elmer Model 56 Recorder and a Perkin-Elmer M-2 Calculating Integrator. A Varian Aerograph Model 9652 Hydrogen Generator was the source of hydrogen. All gas supplies to the GC were filtered with Perkin-Elmer Filter Drier Assemblies.

Reagents. Prepurified grade nitrogen from Union Carbide was used as the carrier gas, and house air was used for the FPD. The calibration standards used were 0.012, 0.030, 0.080% sulfur by weight made by diluting a 0.120% sulfur standard with sulfur-free reference fuel. The blank was sulfur-free reference fuel.

Procedure. The operating parameters for the GC/FPD were as follows: carrier gas, 60 ml/min; air, 100 ml/min; and hydrogen, 150 ml/min.; injection port temperature, 100 °C; oven temperature, 170 °C; detector temperature, 130 °C; manifold temperature, 160 °C. The manifold is not a mixing manifold but is a plumbing area between the column outlet and the detector that is used to direct the column effluent to either or both of the dual detectors in the Perkin-Elmer Model 900 GC. The sample was injected by syringe and in 3–5 min the peak area was printed out on the integrator. A calibration curve was drawn by plotting the logarithm of the concentration as a function of the logarithm of the peak area. The sample concentration was then

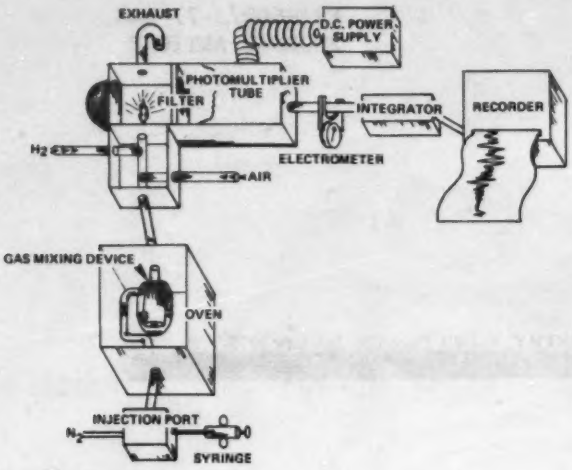

Figure 1. Analytical system

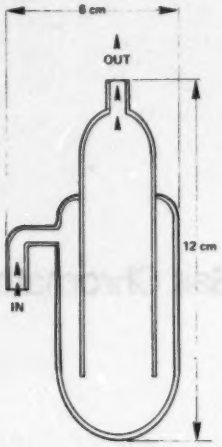

Figure 2. Gas mixing device

read from the calibration curve using the obtained peak area of the sample. All samples, including the calibration standards, were run in duplicate or triplicate.

RESULTS AND DISCUSSION

Hundreds of samples were run by this procedure, most of them in triplicate, over a period of several months. The analysis time for each sample injection was between 3 and 5 min with a detection limit of 0.002% S (by weight) and a precision of ±10% for duplicate results by the same operator. The primary source of error is the imprecision of injection of very small sample volumes (0.1–0.4 μl). This small sample size was necessary to prevent the flame from being extinguished and to keep the samples within the response range of the detector. The extinguishing of the flame by the organic compounds appears to be directly related to operating a hydrogen rich flame (*3*). Also, even with a 0.1-μl sample size, the detector would be saturated with a sulfur concentration above approximately 0.12%. Concentrations of this magnitude were extremely rare, but even these could easily be brought within a workable range by dilution with sulfur-free isooctane or other appropriate solvent. The gas mixing device was also necessary to prevent flame out; and to give a normalized response rather than a spike. Injection of blanks gave no response.

The sensitivity of the FPD as stated above may seem to be very low since the FPD has been used to routinely measure

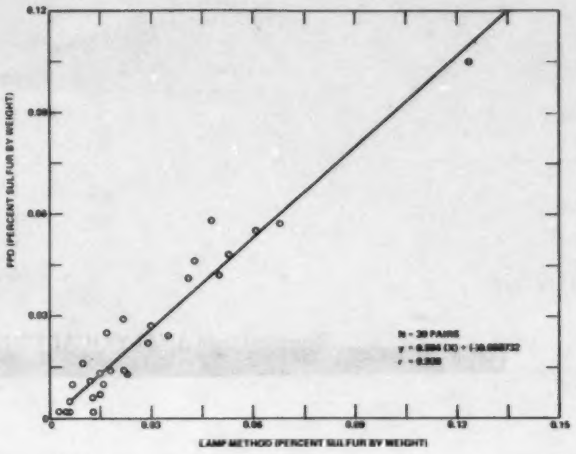

Figure 3. Linear regression curve

Table I. Comparison of Results Obtained by FPD Method and Lamp Method

	% S	
Sample	by FPD	by Lamp Method
A	<0.002 ± 0.0002	<0.01 ± 0.01
B	0.006 ± 0.0006	0.013 ± 0.01
C	0.027 ± 0.0027	0.030 ± 0.01
D	0.046 ± 0.0046	0.043 ± 0.01
E	0.055 ± 0.0055	0.061 ± 0.01

parts per billion levels of some sulfur compounds. But work by Sugiyama, Suzuki, and Takeuchi (*6*) determined that organic compounds entering the FPD with sulfur-containing compounds causes a decrease in the response of the FPD as compared to the response of the FPD when the organic compounds were absent. In characterizing this interference, they found that: (a) the interference by organic compounds increases exponentially with an increase in the concentration of the organic compounds; (b) the interference by an organic compound is independent of the concentration of sulfur-containing compounds; and (c) the decrease in the response of the FPD can be explained by the inactivation of the excited S_2 species by its combination or collision with an organic compound and/or its degradation products. With the procedure described above, the decrease in sensitivity of the FPD is considerable. There is no separation of compounds and the entire gasoline sample or standard enters the FPD at the same time. Since the entire sample is made up of organic compounds and they all enter the FPD at the same time, the effect of the organic compounds on the FPD response is constant. There was also no observable difference in the response of the FPD to different brands or types of gasoline: i.e., leaded–unleaded; high octane–low octane. The use of finished product gasoline from all major manufacturers constitutes the use of all major crudes. Therefore the matrix effect of crudes has been addressed.

All samples were also analyzed by the Lamp Method (*1*). The detection limit of the Lamp Method is 0.01% (by weight) while the detection limit of the FPD method is 0.002%. Precision by the FPD is greater (±10%) than that provided by the Lamp Method (±0.01% sulfur by weight). In addition, the Lamp Method requires a lead correction factor. Over 95% of the results were within the precision limits of the two methods (Table I). The two methods also had a high degree of correlation (Figure 3). Therefore, the stated goals of simplicity,

speed of analysis, and adequate sensitivity were attained. And the results obtained were comparable to the results of an established ASTM method.

Concerning cost of equipment, a GC already owned by a laboratory can be used if it is equipped with an FPD and a gas mixing device, or a very inexpensive GC may be purchased. Even if all the necessary equipment has to be purchased, costs are only a little more than those required for the Lamp Method. Amortization of the equipment can readily be seen in the following rationale: The Lamp Method can analyze 12 samples per man day and a lead correction is necessary. The FPD method can analyze 60 samples per man day and no lead content correction is necessary. A fivefold increase in throughput is anticipated using the same staffing level. At an assumed figure of $80/man day the costs for replacing the Lamp Method by the GC/FPD are amortizable in less than three weeks.

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